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(54) Title: PSEUDOELASTIC BETA TITANIUM ALLOY AND USES THEREFOR

(57) Abstract

A nickel-free beta-titanium alloy containing, in weight percent, between 10.0 and 12.0 percent molybdenum, between 2.8 and 4.0 percent aluminum, between 0.0 and 2.0 percent chromium and vanadium and between 0.0 and 4.0 percent niobium. This alloy possesses pseudo-elastic properties associated with stress-induced martensitic transformation and is suitable for medical uses.

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PSEUDOELASTIC BETA TITANIUM ALLOY AND USES THEREFOR

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REFERENCE TO RELATED APPLICATIONS

This application claims priority from the U.S. Provisional Application, Serial No. 076,922 filed March 5, 1998.

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FIELD OF THE INVENTION

The present invention relates generally to the field of metallurgy and the uses thereof, and, more particularly to shape memory alloys which are particularly suitable for medical uses and which do not use nickel.

15

BACKGROUND OF INVENTION**Shape Memory Effect and Pseudo-elasticity**

Materials which undergo martensite transformation may exhibit "Shape Memory Effect" and "Pseudo-elasticity." During the transformation on cooling, 20 the high temperature phase known as "austenite" changes its crystalline structure through a diffusionless shear process adopting a less symmetrical structure called "martensite", and, on heating, the reverse transformation occurs. The starting temperature of the cooling transformation is referred to as the M_s temperature and the finishing temperature, M_f . The starting and finishing temperatures of

the reverse transformation on heating are referred to as A_s and A_f respectively.

Materials exhibiting Shape Memory Effect can be deformed in their martensitic phase and upon heating recover their original shapes. These materials can also be deformed in their austenitic phase above the A_f temperature through stress-

5 induced martensitic transformation and recover their original shapes upon unloading. This strain recovery, referred to as "pseudo-elasticity" [sometimes referred to herein as "PE"] is associated with the reversion of stress-induced martensite back to austenite. A well known shape memory alloy is nitinol, a near-stoichiometric alloy of nickel and titanium.

10

The Alloy Material

Pure titanium has an isomorphous transformation at 882°C. The body centered cubic (bcc) structure, so called β -Ti, is stable above the isomorphous point and the hexagonal close packed (hcp) structure, so called α -Ti, is stable below.

15

When alloyed with elements such as vanadium, molybdenum, or niobium, the resulting alloys have an extended β phase stability below 882°C. On the contrary, when alloyed with elements such as Al or oxygen, the temperature range of stable α phase extends above the isomorphous point. Elements which have the effect of extending the β phase temperature range are called the β stabilizers while those capable of extending the α phase temperature range are called the α stabilizers.

20

For alloys with a high enough concentration of β stabilizer elements, the material would be sufficiently stabilized to obtain a meta-stable β phase structure

at room temperature. The alloys showing such a property are called β titanium alloys. Martensite transformations are commonly found among β titanium alloys. The M_S temperatures in β -Ti alloys decrease with increasing amount of β stabilizer in the alloys, while increasing amount of α stabilizer raises the M_S .

- 5 The dependence of M_S on the concentration of some transition metals in binary titanium alloys is shown in Figure 14 ['The Martensite Transformation Temperature in Titanium Binary Alloys', Paul Duwez, Trans. ASM, vol. 45, pp.934-940, 1953]. Therefore, depending on the extent of stabilization, β -Ti alloys may exhibit martensitic transformation when cooled very quickly from
- 10 temperatures above the β transus, the temperatures above which β is the single phase at equilibrium.

To exhibit PE at room temperature, the alloys must be sufficiently β stabilized to have the A_f point suppressed to below the ambient, but still allow the formation of stress-induced martensite before plastic deformation occurs. That is,

15 the stress level for the martensite to form must be lower than that of plastic deformation. Shape memory effect, on the other hand, is observed when an alloy has an A_s point higher than and M_S temperature slightly below room temperature. Stress-induced martensite transformations have also been observed in β titanium alloys ['Formation and Reversion of Stress Induced Martensite in

20 Ti-10V-2Fe-3Al', T.W. Duerig, J Albrecht, D. Richter and P. Fischer, Acta Metall., vol. 30, pp.2161-2172, 1982].

Both shape memory effect and pseudo-elasticity have been observed in certain Ti-Mo-Al β titanium alloys ['Shape Memory Effect in Ti-Mo-Al Alloys', Hisaoki Sasano and Toshiyuki Suzuki, Proc. 5th Int. Conf. on Titanium, Munich, Germany, pp.1667-1674, 1984]. In order to obtain SME or PE at room temperature 5 the material has to be properly heat treated to produce the uniform β phase structure. The heat treatment to achieve that goal is called a solution treatment in which the test sample is heated to temperatures slightly above the β transus for a period of time long enough to allow for full austenization and then immediately cooled to room temperature.

10 Some β -Ti alloys, for example, TMA (Registered trade mark of Ormco, Glendora, CA), has been successfully commercialized for orthodontic arch wire application. The detailed description of the applications and properties of β titanium wires can be found in U. S. Pat. No. 4,197,643. The TMA wires show a unique balance of low stiffness, high spring-back, good formability ['Beta 15 titanium: A new orthodontic alloy', C. Burstone and A. Jon Goldberg, American Journal of orthodontics, pp.121-132, Feb. 1980], and weldability. ['Optimal welding of beta titanium orthodontic wires', Kenneth R. Nelson et al, American Journal of Orthodontics and Dentofacial Orthopedics, pp.213-219, Sept., 1987] The nickel-free chemistry of the alloy makes it more tolerable to some patients. However, 20 TMA wires utilize the inherent mechanical properties of the material through thermo-mechanical processing. The material does not exhibit PE due to the occurrence and reversion of stress-induced martensite in the material.

SUMMARY OF THE PRESENT INVENTION

An object of the present invention is to provide a titanium nickel-free SME alloy which is particularly useful for medical applications.

Another object of the present invention is to provide an alloy having pseudo-
5 elastic properties and which is useful for medical applications.

A further object of the present invention is to provide super-elastic springs made from formable, weldable nickel-free shape memory alloy.

Still a further object of the present invention is to provide shape memory orthodontic springs having constant and readily controlled force.

10 Yet a further object of the present invention is to provide nickel-free shape memory or pseudo-elastic compositions for use in orthodontic, maxillo-facial and other surgical applications.

These and other objects of the present invention are accomplished by providing a nickel-free β titanium alloy characterized by exhibiting pseudo-
15 elasticity at -25°C . to 50°C . or greater due to the formation and reversion of stress-induced martensite. Such an alloy exhibits SME at room temperature when the A_S temperature is higher than room temperature. Furthermore, the alloy exhibits pseudo-elasticity with lower stiffness and force output magnitude than the conventional β titanium alloy TMA, better formability than Nitinol, the
20 ability to be welded to other appliances, and good corrosion resistance.

It is capable of being cold worked to 20% without significantly reducing the pseudo-elastic performance, whereby it can be cold formed into various shapes at

ambient temperature while retaining the high spring-back characteristics of the pseudo-elastic phenomenon, and it can be made so that it exhibits pseudo-elasticity at ambient and/or body temperature.

The alloy can have a strain recovery of up to approximately 3.5% when tensile
5 loaded to 4% strain at room temperature in the as-solution treated condition.

The nickel-free β titanium alloy can be used for a medical device within a living body, such as an orthodontic arch wire, a stent, a catheter introducer, oral pins and/or plates used in maxillofacial reconstructive procedures, oviduct clamp, and bone staples, for example. It can also be used for eyeglasses.

10 A nickel-free β titanium having super-elastic properties by being cold worked in its martensitic state, said alloy exhibiting complete elastic behavior at strains up to 4%, thereby permitting the designing of medical instruments and devices which are resistant to permanent deformation or kinking. It can be used for a medical device comprising a small coil capable of being stretched to assume an almost
15 linear shape which allows it to be placed inside a medical catheter for delivery to a desired site in the human body and when discharged from the catheter the wire will assume its original coil form to perform the function of a stent. The composition can be used for a catheter guide wire characterized by great resistance to kinking and possessing excellent torquing (each end twists the same amount,
20 thereby transferring torque accurately).

The nickel-free β titanium alloy may be formed from:

- (a) between 10.0 and 12.0 wt.% molybdenum;

- (b) between 2.8 and 4.0 wt.% aluminum;
 - (c) chromium and vanadium between 0.0 and 2.0 wt.% chromium and vanadium; and
 - (d) between 0.0 and 4.0 wt.% niobium; and
- 5 (e) the balance titanium.

There may be a balanced amount of the alloying elements, and an effective amount of at least one selected from the group consisting of chromium, vanadium and niobium.

In one arrangement it may be formed of molybdenum of 10.2 wt.%,
10 aluminum of 2.8 wt.%, vanadium of 1.8 wt.%, niobium of 3.7 wt.% and the balance of titanium and exhibit pseudo-elasticity between 25 and -25°C.

In another arrangement it may be formed of molybdenum of 11.1 wt.%, aluminum of 2.95 wt.%, vanadium of 1.9 wt.%, niobium of 4.0 wt.% and the balance of titanium and exhibit pseudo-elasticity between 50 and -25°C.

15 It is also a method for making a nickel-free β titanium alloy, comprising the steps of alloying together:

- (a) between 10.0 and 12.0 wt.% molybdenum;
- (b) between 2.8 and 4.0 wt.% aluminum;
- (c) chromium and vanadium between 0.0 and 2.0 wt.% chromium and vanadium; and
- (d) between 0.0 and 4.0 wt.% niobium; and
- (e) the balance titanium.

In this method the alloy can be cold worked up to 20% without significantly

reducing the pseudo-elastic performance, whereby the alloy is capable of being cold formed into various shapes at ambient temperature while retaining the high spring-back characteristics of the pseudo-elastic phenomenon.

Orthodontic Appliances

5 The purpose of orthodontic appliances is to correct teeth irregularities and/or abnormalities in their relationships with surrounding members. This is achieved by using elastically deformed wires which impart forces to the targeted teeth and cause movements during the wire's unloading process.

10 Orthodontic materials have evolved over the years from simple stainless steels to high modulus cobalt alloys, low modulus titanium alloys of linear elasticity and duplex wires using either twisted, braided or coaxial configurations. Materials suitable for orthodontic appliance applications preferably possess a combination of high spring-back, low stiffness, reasonable formability, good corrosion resistance, and the ability to be readily joined to other components.

15 PE phenomenon has not been utilized in orthodontic arch wire application with the exception of NiTi alloy. NiTi, with its exceptionally high strain recovery of up to 8%, has long been used as orthodontic wire material, as was described in U. S. Pat. No. 4,037,324. But the material suffers from poor formability, difficulty in joining with other appliances, and a concern over nickel's toxicity. The 20 availability of a low stiffness pseudo-elastic nickel-free wire with better forming characteristics and the ability to be joined to other appliances would be of great value to the practicing orthodontist.

It has been recognized that optimal tooth motion is accomplished by the

application of a low and constant force on the teeth, thus avoiding root resorption and hyalinization of the periodontal ligament which inhibit tooth motion. The control of the force delivered by the orthodontic appliance can be of two forms, variable cross section wire or variable modulus wires. The latter approach,
5 referred to as variable-modulus technique [C.J. Burstone, American J. Orthodontics, vol. 80, 1981, p1.], has proven more popular with the availability of wires having a wide variety of elasticity and stiffness. Instead of using one type of wire material and varying the desired mechanics by changing the wire dimension, variable-modulus technique has the freedom in selecting wire
10 material which yields the optimum force/deflection characteristics for each stage of the orthodontic practice while maintaining the same wire dimension. This technique significantly reduces appliance complexity and creates greater flexibility in clinical practices.

Stents

15 Stents are fabricated from coiled wire springs or from laser cut tube and are used to repair the patency of previously weakened, narrowed, ballooned or otherwise defective or impaired lumen or other body channels. They are deployed by the use of a catheter in laproscopic procedures. Examples are: blood vessels, bile duct, esophagus, urethra, trachea and the like. Specifically: interluminal lining of
20 Aortic Abdominal aneurysms, iliac or femoral aneurysms, recanalization of injured vessels caused by blunt or penetrating trauma, dilation and recanalization of stenotic arterial segments , tampanade and obliteration of esophageal varices, recanalization of esophageal stenoses secondary to carcinoma or benign strictures,

ureteral strictures and tracheal strictures. In all these applications a nickel free super-elastic or shape memory alloy offers freedom from possible patient reaction to nickel.

5

Catheter Introducers

Interventional cardiovascular procedures require the use of catheters to bring to the area of interest either instruments for measuring and observing the affected area or to deploy stents. The tortuous paths of many of the body vessels require the use of a guiding system to make possible the continuous advance of the catheter; these guide wires are called catheter introducers and two characteristics are required: flexibility and freedom from any tendency to kink and the ability to faithfully transmit a twisting motion from the distal to the proximal end. Super-elastic shape memory alloy wires have demonstrated these characteristics and are the preferred material for construction. It is often desirable to weld to the guide wire some type of ending or handle; the nickel free alloys of the present invention offer weldability far superior to conventional nickel titanium shape memory alloys. In addition, if necessary they can be formed at the operating site to accommodate special requirements of the surgeon.

Oral, Maxillofacial Reconstructive Procedures Using Pins And Plates

Many cosmetic procedures such as reshaping mandible, frontal bones, nose, and cranial features frequently require auxiliary fixtures to support the new position during bone setting. Since in some cases these plates and fixtures may be

left in place, nickel free shape memory or super-elastic alloys would be advantages.

Oviduct Clamp

5 The clamping of a fallopian tube using endoscopic procedures is well established and the use of shape memory clamps is a preferred technique. To avoid the possibility of nickel sensitive reaction, given the long dwell time for such a device, a nickel-free shape memory alloy clamp would provide a drastic reduction in the risk of the procedure.

10 Bone Staples

Shape memory staples have been proposed for bringing into close proximity fractured surfaces of various bones. Healing time is considerably improved by this technique, but questions of tissue reaction remain when using nickel-containing shape memory alloys. A nickel-free shape memory or super-elastic 15 alloy would allay concerns over such a reaction in staples which will have a long dwell time in the body.

The advantages referred to the above noted uses are examples and many other similar surgical devices can benefit from a nickel-free shape memory or PE alloy. 20 Examples of environments in which the alloy of the present invention could be used are disclosed in the following U.S. Patents Nos. 4,503,569 for a graft prosthesis, 5,147,370 for a stent, 5,466,242 for a stent for biliary, urinary or vascular system, 5,653,689 for an infusion catheter, 5,830,179 for a urological stent.

Other objects, features and advantages will be apparent from the following detailed description of preferred embodiments taken in conjunction with the accompanying drawings in which:

5

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the percentages of pseudo-elastic recovery strain relative to the bending strain for the fifteen alloys.

FIG. 2 is a graph showing a tensile stress-strain curve for alloy #42 tested to failure.

10 FIG. 3 is a graph showing stress-strain curves of tensile loading to 4% strain followed by unloading to zero stress of alloy #42 tested at different temperatures.

FIG. 4 is a plot showing the effect of temperature on the first yield of alloy #42.

FIG. 5 is a plot of bend test results of alloy #42 showing the effect of solution treatment temperature on the strain recovery by bending.

15 FIG. 6 is a plot of the pseudo-elastic recovery strain during bend tests of the cold-rolled samples.

FIG. 7 is a plot of pseudo-elastic recovery strains of specimens after aging at 200, 300 and 400° C. against aging time.

20 FIG. 8 is a comparison of the flexural test data of stainless steel, TMA, nitinol and present alloy #42.

FIG. 9 tensile stress-strain curves of alloy #42025 and dogbone specimen of alloy #42.

FIG. 10 tensile hysteresis curves of alloy #42 at three different temperatures.

FIG. 11 yield stress of alloy #42 at different temperatures.

FIG. 12 effect of cold work on the pseudo-elastic strain of alloy #42.

FIG. 13 is a graph of the 15 tensile hysteresis curves of as-solution treated wires of alloy #42025.

5 FIG. 14 is a graph showing the dependence of M_s on the concentration of some transition metals in binary titanium alloys.

FIG. 15 is a graph showing the stress-strain curves of tensile loading to 4% strain followed by unloading to zero stress of alloy X42025 tested at different temperatures.

10

DETAILED DESCRIPTION OF THE INVENTION

All of the sample alloys in the matrix discussed below were prepared by double vacuum arc melting technique. the ingots were hot rolled and flattened to sheets of 1.27 mm in thickness. Oxides on the sheets were removed by double-disc grinding and lapping. The test specimens were cut from sheets and sealed in evacuated quartz tubes back-filled with argon. The capsules were then heater to 15 880° C. for 30 minutes and quenched into a water bath at ambient temperature.

Aging experiments were conducted at 200, 300 and 400° C. using a nitride/nitrate salt bath.

20 Permanent deformation and pseudo-elastic recovery strains were determined by bend tests. Specimens, 0.51 x 1.02 x 51 mm in dimension, were cut from the sheets and then solution treated. After heat treatment, the specimens were bent

against rods of different radii to form a "U" shape. The angles between the straight portions were measured afterwards and the strain recovery calculated to be:

5 $e(\text{rec}) = e(180-\alpha)/180;$

where " α " is the unrecovered angle and " e " is the outer-fiber bending strain.

Tensile strain recovery was measured by tensile elongation to 4% strain followed by unloading to zero stress. Dogbone tensile specimens with a cross 10 sectional dimension of 0.90 mm x 2.0 mm were used and the strain was monitored using an extensometer. An environmental chamber with electrical heating and CO₂ cooling capabilities provides a range of test temperature from - 30° C. to 180° C.

The bending moment/deflection characteristics of orthodontic wire were 15 determined by flexural tests at a university laboratory. Specimens 0.41 x 0.56 mm in cross section were used. A torque gauge apparatus was used to apply an angular deflection to the wires. The angular deflection of the specimens was measured with a protractor. The couple necessary to create the angular displacement was resisted by a force at the free end through an anvil placed 20 against the specimens. A 5mm span length was used for all the tests.

Bend tests at 6% bending strain were used for screening the alloys for their pseudo-elastic properties. The percentages of pseudo-elastic recovery strain relative to the bending strain for the fifteen alloys (one alloy was out-of-range and therefore was not used) are plotted in FIG. 1. Among the alloys, #42 exhibited the

highest pseudo-elastic strain recovery and was selected for further studies.

FIG. 2 shows a tensile stress-strain curve of alloy #42 tested to failure. The mechanical properties based on the curve are summarized in Table I. In absence of significant work hardening, the reduction in cross-section area (R.A.) is much higher than the tensile elongation and is a better indication of the true ductility of the alloy.

10

Table I. Mechanical properties of alloy #42.

UTS	Yield Stress	Young's Modulus	R.A.	Tensile Elongation
765MPa	500MPa	65 GPa	27%	13.7%

Tensile loading/unloading hysteresis curves for alloy #42 tested to 4% strain at temperatures from -25° C. to 150° C. are shown in FIG. 3.

15

A matrix of fifteen β titanium alloys with the composition range (wt.%) listed

in Table II. were examined.

Table II.

	Mo	Al	Cr	V	Nb
Low	9.5	2	0	0	0
High	12	4	2	2	4

20

The alloys use molybdenum as the major β stabilizer and aluminum as the

major α stabilizer. Their chemical compositions are listed in Table III. All

specimens were subjected to a standard solution treatment of 10 minutes at 800°C followed by quenching into a water bath at room temperature. Bend test results of

as-solution treated specimens in Table III. show the alloys which exhibit SME or PE at room temperature. Out of the fifteen alloys screened, alloys #28, 32, 37, and 42 exhibited significant pseudo-elastic strain recovery, while alloys #31, 33 and 41 exhibited SME.

5

Table III.

Alloy ID	Mo	Al	Cr	V	Nb	ES (%)	SME (%)	PD (%)
27	9.5	3.1	1.4	1.4	3.1	1.6	0	4.3
28	10.0	3.5	1.7	0	0	3	0	2.9
29	9.0	2.3	1.4	0	3.0	2	0.1	4
30	10.3	2.7	1.8	1.6	0	2.3	0.1	3.7
31	11.8	3.7	0	0	0	1.9	3.5	0.7
32	11.0	2.8	0	1.8	3.6	3.1	0.1	3.1
33	10.4	3.6	0	1.8	3.7	1.7	3.8	0.9
34	10.2	2.7	0	0	0	2.1	0	3.4
35	11.5	3.7	1.8	0	0	1.8	0	3.8
36	8.4	3.0	1.4	1.4	3.0	2	0.1	4
37	11.6	2.8	1.8	1.8	0	3.4	0	2.5
38	10.4	2.6	1.8	1.8	3.7	2.3	0.1	3.5
39	11.6	3.6	0	1.8	3.8	2.6	0.1	3.7
41	11.5	2.8	0	0	0	1.8	3.5	0.5
42	10.2	2.8	0	1.8	3.7	3.7	0.5	2.2

ES - elastic spring-back

10 SME - shape memory strain recovery on heating

PD - permanent plastic deformation

The tensile loading-unloading test gives accurate quantitative results on strain recovery and modulus, and therefore is a widely accepted way of characterizing materials exhibiting SME and PE. Stress-strain curves of tensile loading to 4% strain followed by unloading to zero stress tests on alloy #42 are shown in FIG. 3. Distinctive PE was observed in the temperature range between -25 and 25°C. Effects of cold work on the PE of alloy #42 were also studied by bend tests. The

bend test results indicate that cold work up to 20% of as-solution treated specimens does not affect the strain recovery significantly (FIG. 3) where the temperatures range from -25° C. to 150° C. well defined pseudo-elasticity was observed at temperatures below 25° C. The residual plastic deformation decreases 5 as pseudo-elasticity becomes more pronounced with decreasing temperatures. The yield stress (critical stress to induce martensite) is relatively insensitive to the temperature as it decreases only slightly with decreasing temperature (FIG. 4).

The bend test results of #42 after solution-treatment at 880° C., 830° C. and 780° C. for 30 minutes are shown in FIG. 5. Specimens heat treated at temperatures 10 lower than 880° C. resulted in lower amount of pseudo-elastic strain recovery.

Solution-treated sheets of alloy #42 were cold rolled to thicknesses with 10% and 20% reduction. The pseudo-elastic recovery strain during bend tests of the cold-rolled samples are plotted in FIG. 6. It can be seen that pseudo-elastic strain recovery decreases only slightly as a result of increasing amount of cold work, 15 indicating that pseudo-elasticity in this alloy is not significantly affected by cold deformation up to 20%.

Effects of aging at temperatures from 200 to 400° C. were studied by bend tests to 4% total outer-fiber bending strains. Pseudo-elastic recovery strains of specimens after aging at 200, 300 and 400 ° C. are plotted against aging time in FIG. 20 7. The pseudo-elastic recovery strain decreases from the as-solution-treated level of 2.8% to approximately 1.5% after one day of aging at 200° C. and to about 1.8% after five hours of aging at 300° C. It was also noted that ductility of the alloy

decreases significantly during aging at these temperatures. The reductions in area measured after tensile test specimens with selected aging condition are listed in Table IV. Bend test specimens after aging at 300° C. for 600 minutes and 400° C. for 1000 minutes broke at 4% bending strain during the tests.

5

Table IV. Area (R.A.) of alloy #42 after aging treatment.

Aging Treatment	R.A.
200° C./50 hrs.	12.6%
300° C./60 min.	14.1%
300° C. /100 min.	9.5%

The aging embrittlement at these low temperature is most likely related to the
10 formation of ω -phase as two of the effects of ω -phase observed by Duerig et al, i.e.,
low work hardening and low ductility, are also observed in the specimens aged at
200 and 300° C.

The tensile stress-strain curves of alloy #42 as well as 0.4mm diameter wire of
alloy #42025 tested to failure are shown in FIG. 9. The tensile elongation of the
15 #42025 specimen in the as-solution-treated condition is approximately 7 percent
which is approximately half of what was obtained from #42 specimen. The
ultimate tensile strength of the wire specimen is about 1000 MPa, significantly
higher than that of #42, which is around 780 MPa. The mechanical properties
based on the test data are summarized in Table I. In the absence of significant
20 work hardening, the reduction in cross-section area (R.A.) is much high than the
tensile elongation and is a better indication of the true ductility of the alloy.

Tensile hysteresis curves tested to 4% strain at temperatures at -25, 25 and 100° C. are shown in FIG. 10. Well defined pseudo-elasticity was observed at temperatures below 25° C. The yield stress (critical stress to induce martensite) is relatively insensitive to the temperature as it decreases only slightly with 5 decreasing temperature (FIG. 11). This indicates that the A_f point of this alloy is below room temperature and M_d , the temperature above which PE cannot take place, is close to 100° C.

Solution-treated sheets of alloy #42 were cold rolled to thickness with 10% and 20% reduction. The pseudo-elastic recovery strain by bend tests of samples with 10 and without cold work are plotted in FIG. 12. It can be seen that pseudo-elastic strain recovery decreases only slightly as a result of increasing amount of cold work, indicating that pseudo-elasticity in this alloy is not significantly affected by cold deformation up to 20%.

The new alloy, X42025, based on the composition of alloy #42 was melted and 15 processed to wires of 0.061" and 0.016" diameter. The wet chemical analysis showed that the alloy has a chemical composition of : Ti- 11.14 wt.% Mo- 2.95 wt.% Al- 1.88 wt.% V- 3.99 wt.% Nb. The tensile loading to 4% strain followed by unloading to zero stress curves of alloy X42025 are shown in Figure 15. Again, the alloy exhibits distinct PE between -25°C and 50°C.

20 Comparing the chemical compositions of alloys #42 and X42025, it is noted that even though the composition of molybdenum in X42025 is almost one

percent higher than that of alloy #42, both exhibit significant PE in a quite similar temperature range. Since the martensite transformation temperatures are very sensitive to the molybdenum content, it is clear that a wide A_f range exists for the alloys to exhibit PE at room temperature. By examining the chemical compositions of alloys with PE or SME, it is recognized that alloys with chemical compositions within the boundaries of: molybdenum between 10.0 and 12.0 wt.%, aluminum between 2.8 and 4.0 wt.%, chromium and vanadium between 0.0 and 2.0 wt.%, and niobium between 0.0 and 4.0 wt.%, would exhibit PE or SME when the transformation temperatures, decided by the proper balance of α and β stabilizers, fall in the right temperature range. With the experimental data available one skilled in the art can define the transformation temperature or operating temperature range required for either SME or PE.

Solution-treated sheets of alloy #42 were cold rolled to thickness with 10% and 20% reduction. The pseudo-elastic recovery strain by bend tests of samples with and without cold work are plotted in FIG. 12. It can be seen that pseudo-elastic strain recovery decreases only slightly as a result of increasing amount of cold work, indication that pseudo-elasticity in this alloy is not significantly affected by cold deformation up to 20%.

A good way to compare the mechanical performance between pseudo-elastic β titanium and other commercial orthodontics arch wire materials is by the flexural test. Flexural tests produce the bending moment - activation angle curves which allow us to compare the relative force output, stiffness and spring-back among different wire materials; and therefore is important for the quantitative

evaluation of a new alloy for orthodontic applications. Flexural tests provide a direct comparison of bending moment-activation angle relationship among a variety of arch wire materials, which is an important quantitative evaluation of a new alloy for the application of orthodontic arch wire. The flexural test curves of 5 18-8 stainless steel, Nitinol, TMA and alloy #42 of FIG. 8 indicates that alloy #42 has a combination of desirable characteristics. Alloy #42 has a spring-back characteristic comparable to that of TMA, which is between those of stainless steel and Nitinol. The force output, on the other hand, is similar to that of Nitinol. The data suggested that alloy #42 has the desirable combination of the following 10 properties, a similar spring-back characteristics together with a lower stiffness when compared to those of TMA and better formability than that of Nitinol.

A detailed description of the test setup and method can be found in previous literature. ['Chinese NiTi wire-A new orthodontic alloy', by Charles J. Burstone et al, American Journal of Orthodontics, pp. 445-452, June, 1985] Flexural test curves 15 of 18-8 stainless steel, Nitinol, TMA and alloy #42 are depicted in Figure 8. The flexural test data indicates that alloy #42 has a combination of the following properties; a similar spring-back characteristics together with a lower stiffness when compared to those of TMA and better formability than that of Nitinol.

Part of the #42025 forged bar was cold drawn with inter-pass vacuum 20 annealing down to wires of 1.52mm and 0.40mm in diameter with approximately 30% retained cold reduction in cross-section area. The pilot size trial for the production of alloy #42025 demonstrated that the alloy can be successfully processed to the desired size for orthodontic applications. The room temperature

tensile hysteresis curves of 0.40mm and 1.52mm diameter wires in the as-quenched condition are shown in FIG. 13. Distinct pseudo-elasticity can be seen on the curve of 1.52mm wire but almost nonexistent on the 0.40 mm wire curve.

A layer of contaminated structure was observed on the surface of the 0.40mm
5 wire but not on 1.52mm wire sample. The surface layer of a piece of 0.40 wire was mechanically polished to approximately 0.30mm diameter followed by solution treatment in argon. The resulting tensile hysteresis curve showed some improvement in pseudo-elasticity (FIG. 13).

The surface layer is believed to be α phase caused by oxygen infiltration during
10 hot processing in air and is detrimental to the pseudo-elasticity of the alloy. Therefore, the production process needs to avoid extended high temperature exposure in any oxygen-containing atmosphere, especially in the latter stage of wire drawing to obtain materials with high pseudo-elastic springback for the orthodontic applications.

15 Comparing the tensile hysteresis curves of #42 and 1.52mm diameter wire of #42025, it is believed that , with optimized composition as well as a proper production and heat treating process, this material significantly improves its pseudo-elastic properties making it a more versatile and competitive material in orthodontic, and other medical applications.

20 Alloy #42 as well as alloys of its class has a unique place in orthodontic usage. It is highly formable without adverse effect on pseudo-elasticity which allows the fabrication of complex anchors, loops, and springs and their modification at chairside by the orthodontist to individualize treatment. Steel and titanium

wires are also formable; however their force levels are much higher for full wire-attachment engagement. Alloy #42 has applications in initial leveling or alignment where moderate discrepancies exist, low forces are needed, and bends are placed to reduce side effects, overtreat, and to individualize arch forms.

5 Thus, a pseudo-elastic titanium alloy based on Ti-Mo-Al has been developed. The alloy, when properly solution treated, exhibits a well-defined pseudo-elastic behavior which is insensitive to decreasing temperature below the ambient. The pseudo-elastic behavior of the alloy is not significantly affected by cold work up to 20% reduction. Aging of the present alloy at temperatures in the range of 200 to
10 400° C. results in decrease of pseudo-elastic strain recovery and loss in ductility. The alloy possesses desirable properties of good spring-back, low stiffness, and good formability for orthodontics arch wire application. When compared with other commercial orthodontics arch wires, the present alloy exhibits spring-back similar to that of TMA and stiffness similar to that of nitinol. Orthodontics arch
15 wires of the present alloy is ideal for the intermediate stage of orthodontic treatment.

It will now be apparent to those skilled in the art that other embodiments, improvements, details and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by
20 the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

We claim:

1 1. A nickel-free β titanium alloy characterized by exhibiting pseudo-elasticity
2 at -25° C. to 50° C. due to the formation and reversion of stress-induced
3 martensite.

1 2 A nickel-free β titanium alloy as defined in claim 1, which exhibits SME at
2 room temperature when the A_S temperature is higher than room temperature.

1 3. A nickel-free β titanium alloy as defined in claim 1 which exhibits pseudo-
2 elasticity with lower stiffness and force output magnitude than the conventional
3 β titanium alloy TMA, better formability than Nitinol, the ability to be welded to
4 other appliances, and good corrosion resistance.

1 4 A nickel-free β titanium alloy as defined in claim 1 capable of being cold
2 worked to 20% without significantly reducing the pseudo-elastic performance,
3 whereby it can be cold formed into various shapes at ambient temperature while
4 retaining the high spring-back characteristics of the pseudo-elastic phenomenon.

1 5. A nickel-free β titanium alloy as defined in claim 1 which exhibits pseudo-
2 elasticity between 25 and -25°C.

1 6. A nickel-free β titanium alloy as defined in claim 1 which exhibits pseudo-
2 elasticity at ambient and/or body temperature.

1 7. A nickel-free β titanium alloy as defined in claim 5, which has a strain
2 recovery of approximately 2.7% when tensile loaded to 4% strain at room
3 temperature in the as-solution treated condition.

1 8. A nickel-free β titanium alloy as defined in claim 6, which has a strain
2 recovery up to approximately 3.5% when tensile loaded to 4% strain at room
3 temperature in the as-solution treated condition.

1 9. A nickel-free β titanium alloy as defined in claim 1 used as an orthodontic
2 arch wire, springs, implants, endodontic files and other orthodontic devices.

1 10. A nickel-free β titanium alloy as defined in claim 1 used for eyeglasses.

1 11. A nickel-free β titanium alloy as defined in claim 1 used for a medical
2 device within a living body.

1 12. A nickel-free β titanium alloy as defined in claim 11 wherein said medical
2 device is chosen from the following group: (1) a stent; (2) a catheter introducer; (3)
3 oral pins and/or plates used in maxillofacial reconstructive procedures; (4)
4 oviduct clamp; and (5) bone staples.

1 13. A nickel-free β titanium alloy as defined in claim 1 characterized
2 by having super-elastic properties by being cold worked in its
3 martensitic state, said alloy exhibiting complete elastic behavior at

4 strains up to 4%, thereby permitting the designing of medical
5 instruments and devices which are resistant to permanent deformation
6 or kinking.

1 14. A nickel-free β titanium alloy as defined in claim 13 used for a
2 medical device comprising a small coil capable of being stretched to
3 assume an almost linear shape which allows it to be placed inside a
4 medical catheter for delivery to a desired site in the human body and
5 when discharged from the catheter the wire assuming its original coil
6 form to perform the function of a stent.

1 15. A nickel-free β titanium alloy as defined in claim 13 used for a
2 catheter guide wire characterized by great resistance to kinking and
3 possessing excellent torquing (each end twists the same amount,
4 thereby transferring torque accurately).

1 16. A nickel-free β titanium alloy as defined in claim 1 characterized
2 by good corrosion resistance and good bio-compatibility as exhibited by
3 alloys in the NiTi SME alloy family.

1 17. A nickel-free β titanium alloy as defined in claim 1, comprising:
2 (a) between 10.0 and 12.0 wt.% molybdenum;
3 (b) between 2.8 and 4.0 wt.% aluminum;
4 (c) chromium and vanadium between 0.0 and 2.0 wt.% chromium and

- 5 vanadium; and
6 (d) between 0.0 and 4.0 wt.% niobium; and
7 (e) the balance titanium.

1 18. A nickel-free β titanium alloy as defined in claim 17, there being a
2 balanced amount of the alloying elements, and an effective amount of at
3 least one selected from the group consisting of chromium, vanadium and
4 niobium.

1 19. A nickel-free β titanium alloy as defined in claim 18, comprising,
2 molybdenum of 10.2 wt.%, aluminum of 2.8 wt.%, vanadium of 1.8 wt.%,
3 niobium of 3.7 wt.% and the balance of titanium and exhibiting pseudo-elasticity
4 between 25 and -25°C.

1 20. A nickel-free β titanium alloy as defined in claim 18, comprising
2 molybdenum of 11.1 wt.%, aluminum of 2.95 wt.%, vanadium of 1.9 wt.%,
3 niobium of 4.0 wt.% and the balance of titanium and exhibiting pseudo-elasticity
4 between 50 and -25°C.

1 21. A method for making a nickel-free β titanium alloy, comprising the steps
2 of alloying together:
3 (a) between 10.0 and 12.0 wt.% molybdenum;
4 (b) between 2.8 and 4.0 wt.% aluminum;
5 (c) chromium and vanadium between 0.0 and 2.0 wt.% chromium and

6 vanadium; and

7 (d) between 0.0 and 4.0 wt.% niobium; and

8 (e) the balance titanium.

1 22. A method as defined in claim 21, wherein the alloy is cold worked up to
2 20% without significantly reducing the pseudo-elastic performance, whereby the
3 alloy is capable of being cold formed into various shapes at ambient temperature
4 while retaining the high spring-back characteristics of the pseudo-elastic
5 phenomenon.

1 23. A method as defined in claim 21, further comprising the step of forming
2 the alloy into an orthodontic arch wire.

1 24. A method as defined in claim 21, further comprising the step of using the
2 alloy for making eyeglasses.

1 25. A method as defined in claim 21, further comprising the step of forming
2 the alloy into a medical device within a living body.

1 26. A method as defined in claim 21, wherein said medical device is chosen
2 from the following group: (1) a stent; (2) a catheter introducer; (3) oral pins and/or
3 plates used in maxillofacial reconstructive procedures; (4) oviduct clamp; and (5)
4 bone staples.

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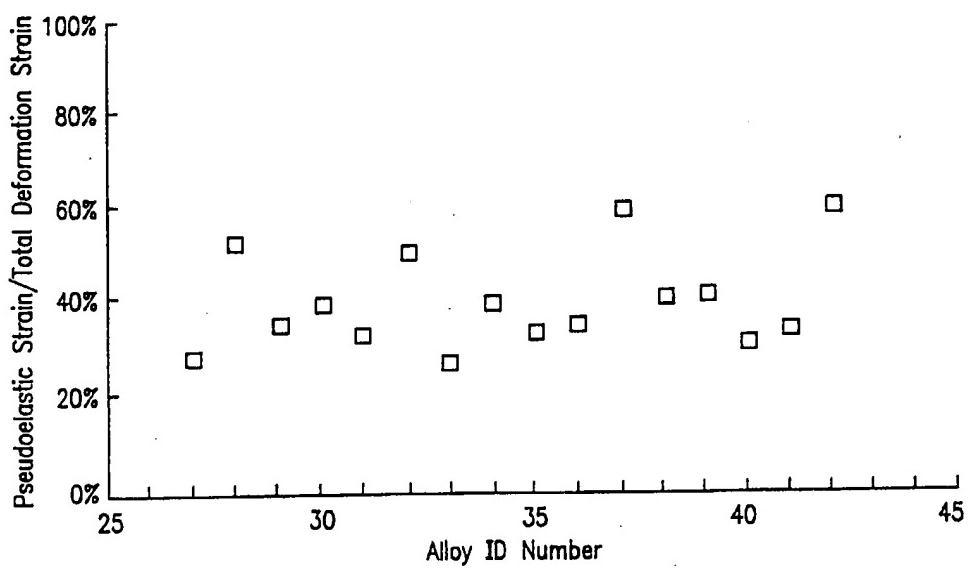


FIG. 1

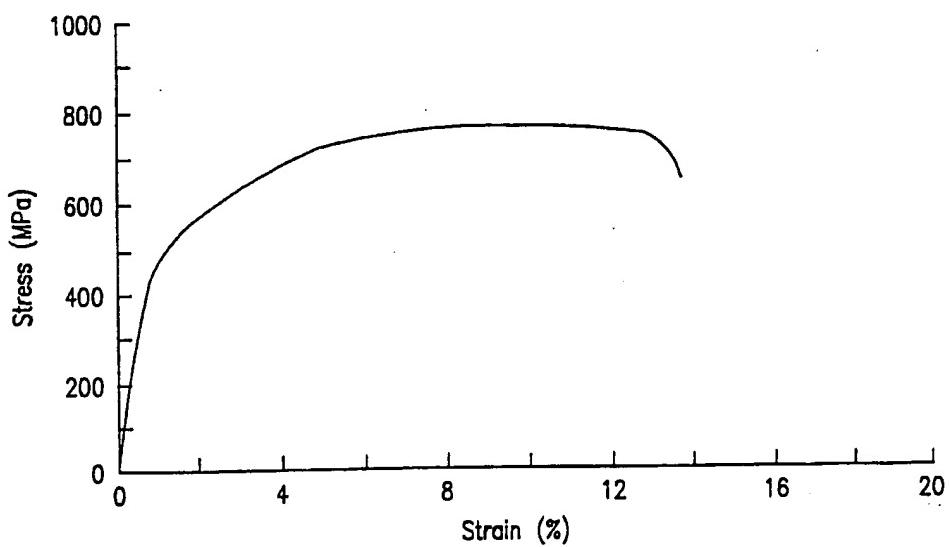


FIG. 2

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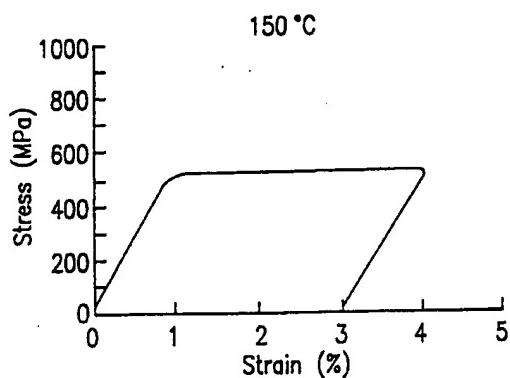


FIG. 3A

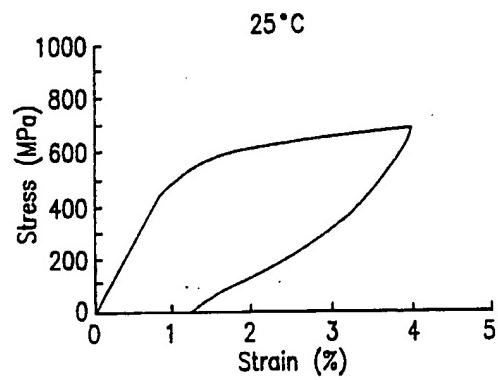


FIG. 3D

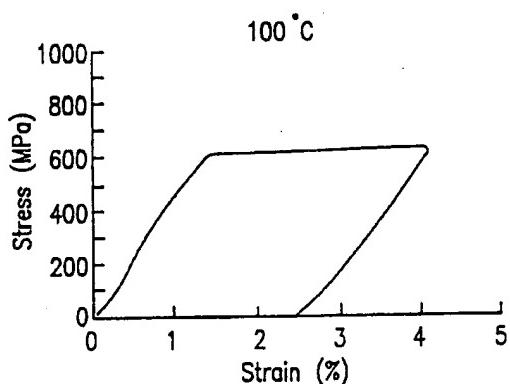


FIG. 3B

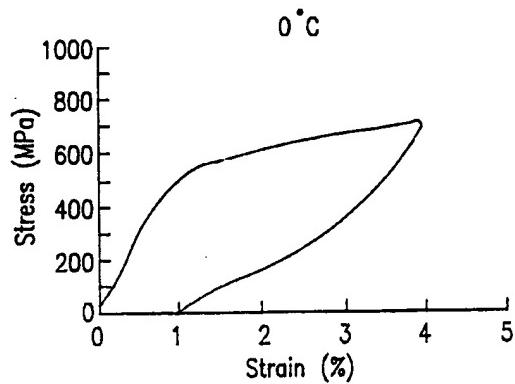


FIG. 3E

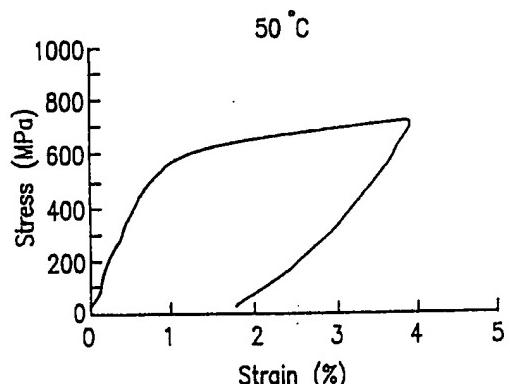


FIG. 3C

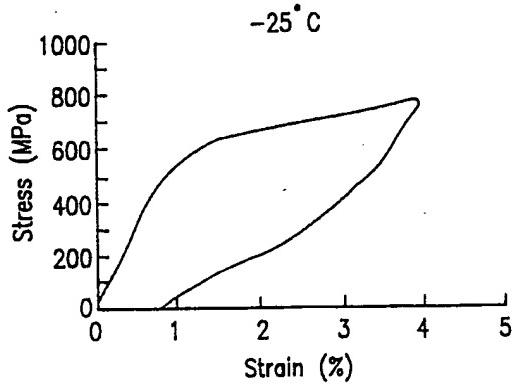


FIG. 3F

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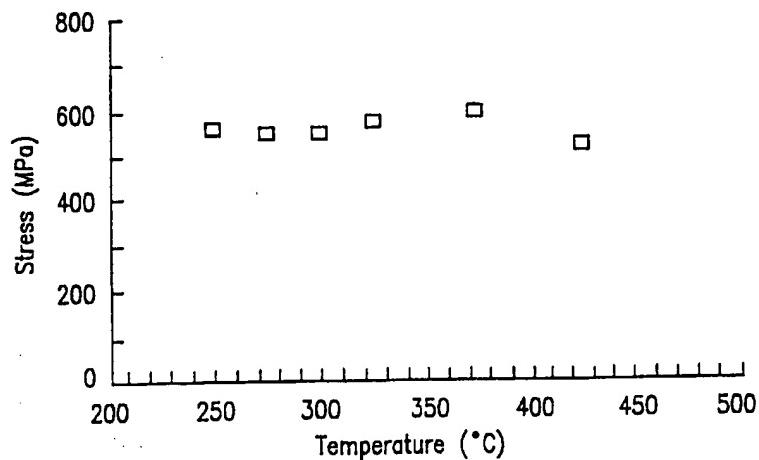


FIG. 4

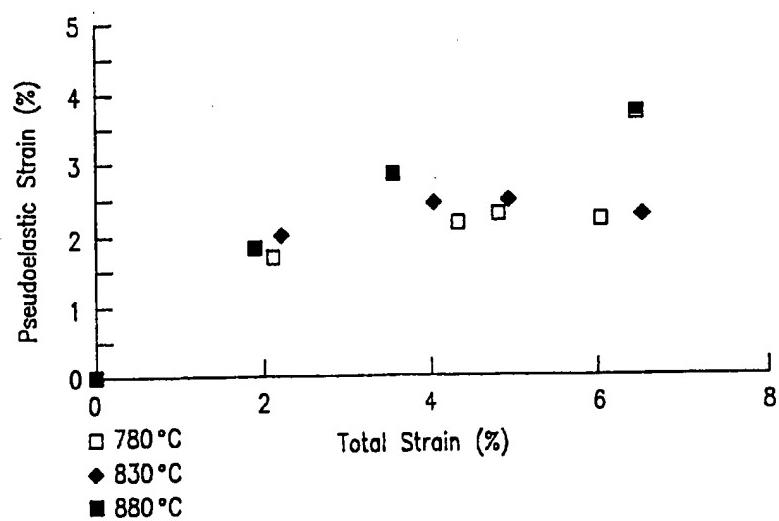


FIG. 5

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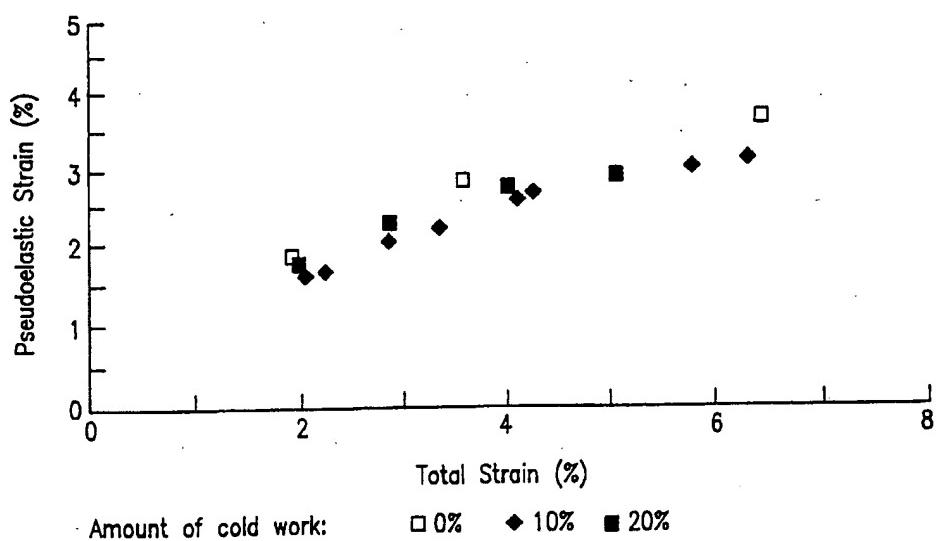


FIG. 6

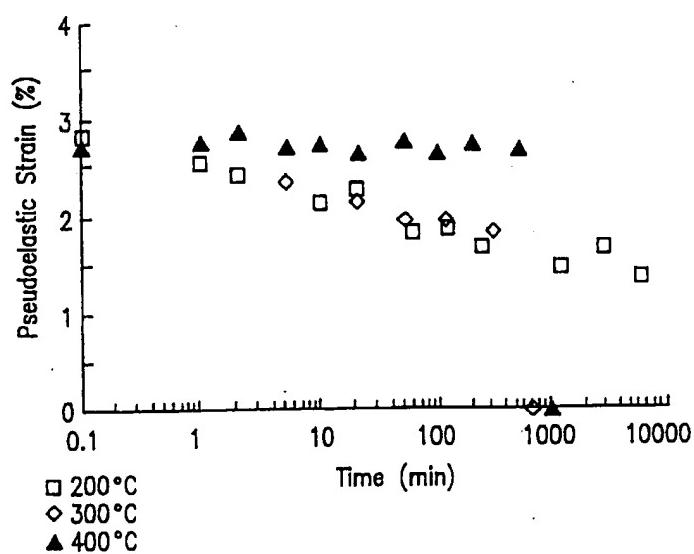


FIG. 7

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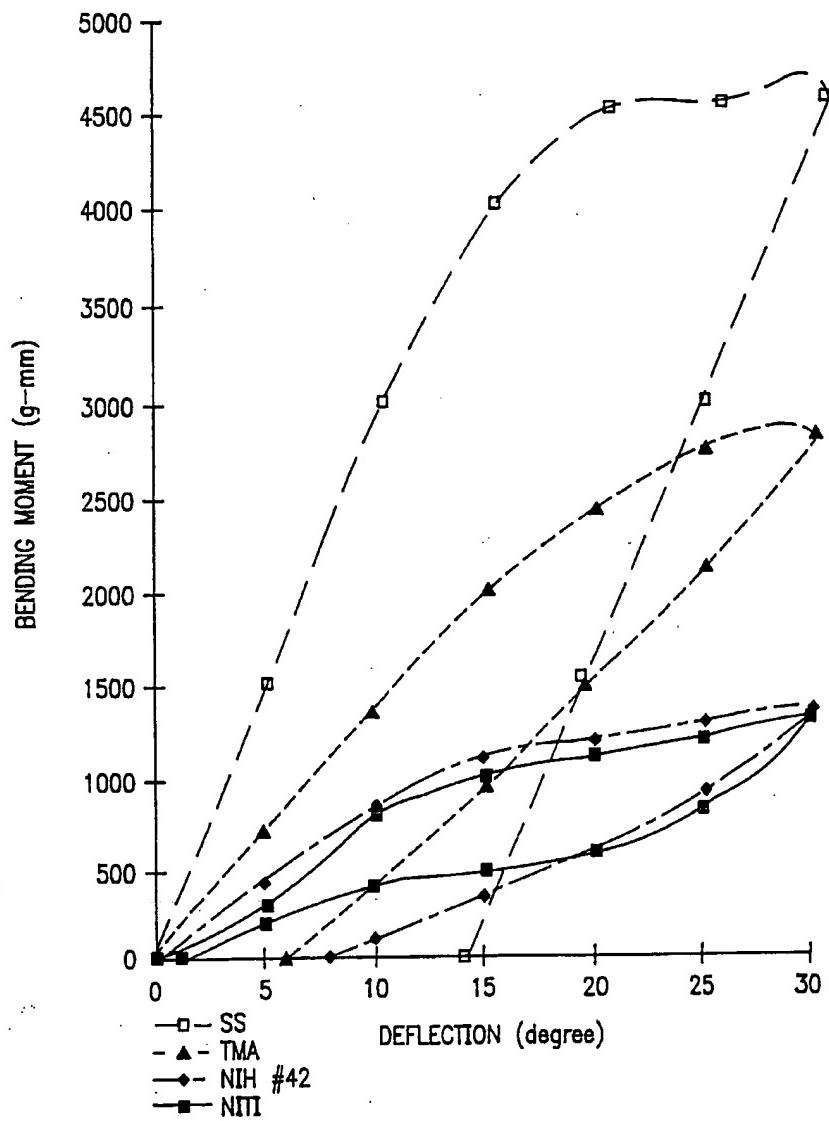


FIG. 8

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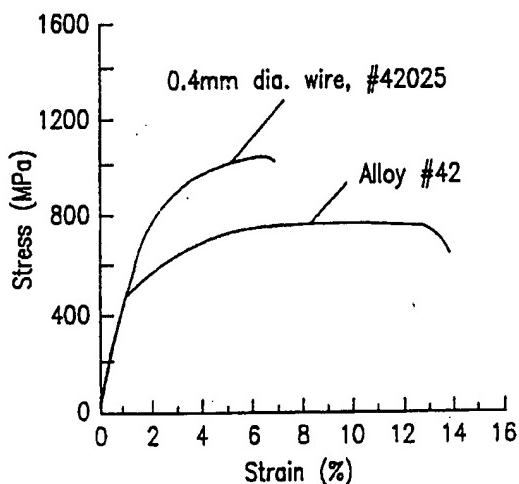


FIG. 9

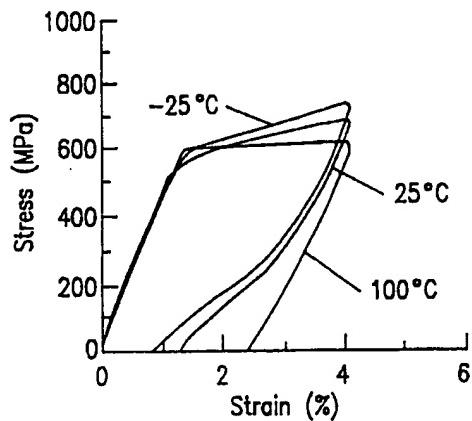


FIG. 10

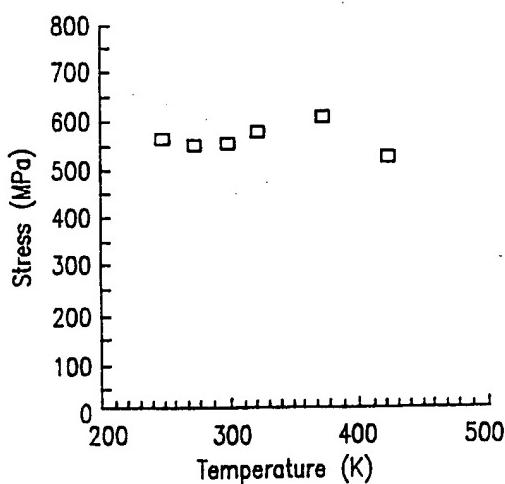


FIG. 11

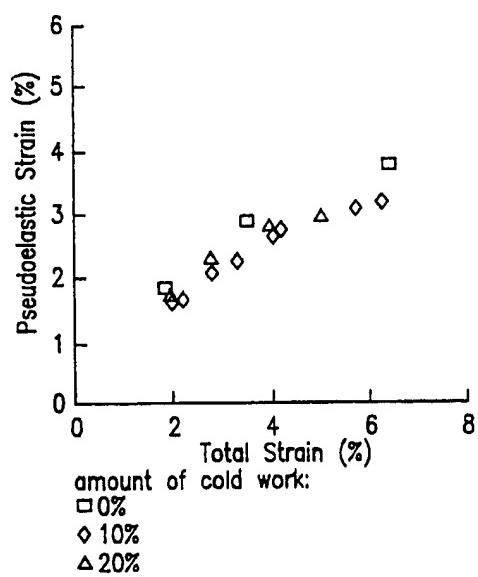


FIG. 12

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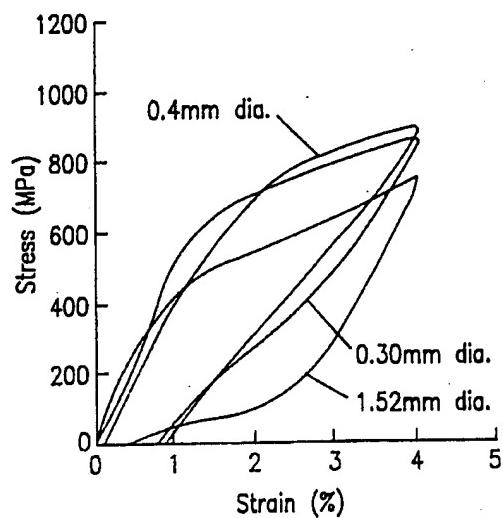


FIG. 13

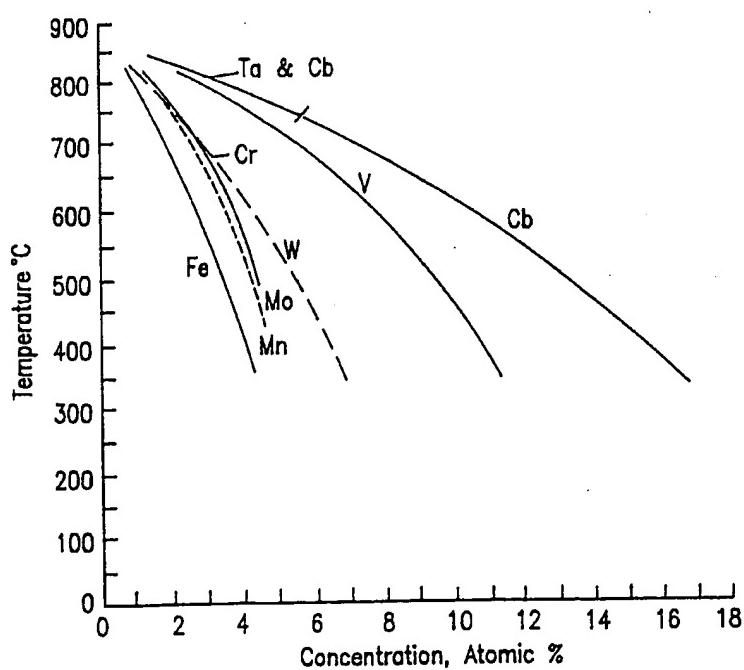


FIG. 14

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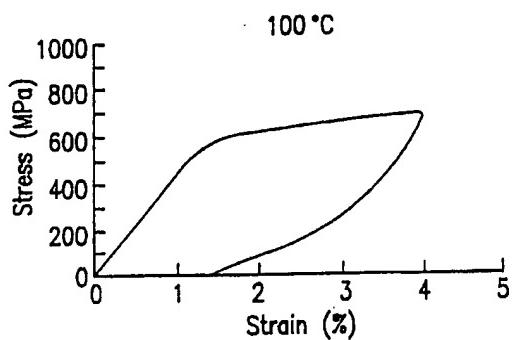


FIG. 15A

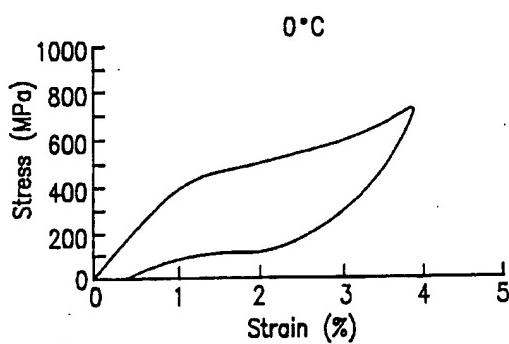


FIG. 15D

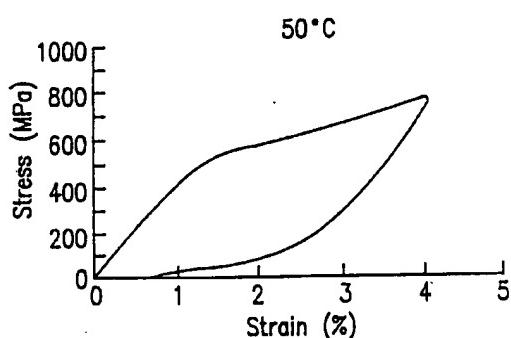


FIG. 15B

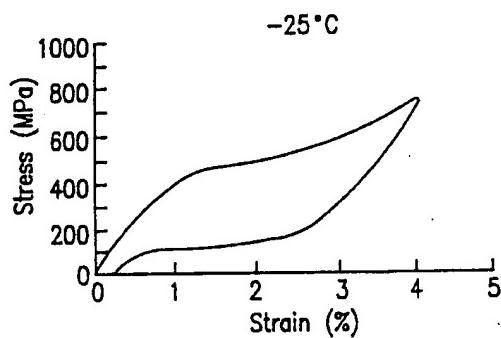


FIG. 15E

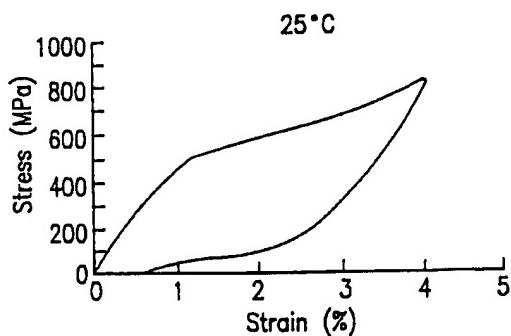


FIG. 15C

INTERNATIONAL SEARCH REPORT

International application No. PCT/US99/04901

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C22C 14/00; C22F 1/18

US CL :148/421, 669, 670, 671; 420/417, 418, 421

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/421, 669, 670, 671; 420/417, 418, 421

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS-FILE EPO, FILE JPO and FILE USPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,409,015 A (PALERMO) 25 April 1995.	1-26
Y	US 5,264,055 A (CHAMPIN et al.) 23 November 1993, column 1, lines 43-55.	1-26
Y	US 4,952,236 A (WANG et al.) 28 August 1990, column 3, lines 40-45.	1-26
A	US 5,069,226 A (YAMAUCHI et al.) 3 December 1991.	1-26
A	US 4,253,873 A (SAGOI et al.) 3 May 1981.	1-26
A	US 4,197,643 A (BURSTONE et al.) 15 April 1980.	

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"		document defining the general state of the art which is not considered to be of particular relevance
"E"	"X"	earlier document published on or after the international filing date
"L"		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"		document referring to an oral disclosure, use, exhibition or other means
"P"	"&"	document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search	Date of mailing of the international search report
27 MAY 1999	21 JUN 1999

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JOHN P. SHEEHAN Telephone No. (703) 308-0651
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